PREVENTION MECHANISM OF EXPLOSIVE OF AIR-METHANE MIXTURE BY SALT INHIBITORS

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Abstract

The most perspective direction of increasing the protecting property level of explosives is the usage of new chemically active inhibitor salts in their mixtures. However, we have no adequately clear understanding of the mechanism of the inhibition reactions taking place in air-methane mixtures under the explosion of an explosive charge. That's why the identification of this mechanism is a problem that is of great scientific and practical importance.

Abstrakt

Nejperspektivnějším směrem zvyšování úrovně ochranné vlastnosti trhavin je použití nových chemicky aktivních solí inhibitorů v jejich směsích. Nicméně chybí dostatečně jasné pochopení mechanizmu inhibičních reakcí probíhajících ve směsích metanu se vzduchem při explozi trhací nálože. Proto identifikace tohoto mechanizmu představuje důležitý vědecký a praktický problém.

INTRODUCTION

The analysis of the last researches and publications shows that the variety of views of the process of air-methane mixture inflammation during the explosion of a charge did not shake the basic concepts of the N.N. Semenov's theory that the stopping of detonation or burning of explosive methane mixture was connected with a breakage of chains of intermediate chemical reactions and depended on the mass of the added salt-inhibitor to the mixture and on the size of its part. The breaking of the chains of the intermediate chemical reactions at the time of the air-methane mixture inflammation occurred as a result of the recombination process of active centers-radicals by the inhibitor on the surface of salt parts. The elucidation of the mechanism is the basic key in solving the problem of explosive's safety.

The aim of this work is to discuss the recombination mechanism of radicals by a salt - inhibitor that is possible at the time of the charge explosion in the air-methane mixture. It is necessary for the grounded choice of the most effective salt inhibitors that are intended for high prevention explosives.

ANALYTICAL INVESTIGATIONS

In the work [1] there is offered to examine the conditions of explosive safety under which the air-methane mixture charge could be safe as a process where the methane inflammation probability was determined by the quantity of radicals having been formed at the time of the charge explosion on the one hand and by the quantity of their recombination by a salt inhibition on the other hand. In this case any air-methane mixture inflammation is impossible if the quantity of the recombination acts of active centers by inhibitors reaches such value that the quantity of radicals in the zone of the air-methane mixture reaction, prepared for the charge, is lower than the critical one. Thus the higher the heat of explosion of permissible explosives – Q_{BB} is that is transmitted to the air-methane mixture, the greater the quantity of active centers-radicals is; and the higher the concentration of the salt-inhibitor in detonation products – β is, the greater the quantity of acts of the active center recombination take place on the surface of the parts of the salt-inhibitor.

According to the work [1] the index of safety – *P* determining the level of preservative properties of permissible explosives is defined as follows:

$$P = \beta \cdot I \cdot Q_{VV}^{-1}, \tag{1}$$

where *I* is an inhibition ability of salt;

$$I = \frac{F \cdot S}{M_V}, \tag{2}$$

F - chemical factor of salt activity;

S - elementary surface of salt particles;

M_V - molecular weight of salt-inhibitor.

The heat of explosion of permissible explosives, being transmitted to the air-methane mixture at the time of the charge explosive detonation also depends on the salt-inhibitor content in the explosive and can be marked according to the formula:

$$Q_{VV} = Q_V \sqrt{1-\varepsilon}, \tag{3}$$

where Q_V is a potential specific heat of explosion of permissible explosives;

ε is an abundance of salt-inhibitor in the content of permissible explosives (in content of explosion products).

If we express the mass of salt-inhibitor through the quantity of moles – n_I and its molecular weight (M_V) and refer all magnitudes to 1 kg of the explosive then considering the equations (2) and (3) we get the equation of the index P according to the equation (1) in the following way:

$$P = \frac{n_u \cdot M_V}{V_{PV}} \cdot \frac{F \cdot S}{M_V} \cdot (Q_V \sqrt{1-\frac{n_u \cdot M_V}{1000}})^{-1} = \frac{4{,}464 \cdot 10^{-2} \cdot n_u \cdot F \cdot S}{N_{PV} \cdot Q_V \cdot \sqrt{(1-\frac{n_u \cdot M_V}{1000})}}, \tag{4}$$

where N_{PV} - mole quantity of gaseous explosion products, mole/kg;

Q_V - specific potential energy of explosive detonation, kilojoules /kg;

S - specific surface of parts of salt-inhibitor, m^2/kg.

It is evident that the chemical factor of salt activity *(F)* determines its ability to recombine radicals and to inhibit chain oxidation reaction of methane according to the chemical nature of elements making salt-inhibitor. The chemical process of the recombination of radicals taking place on the surface of a crystal of the salt-inhibitor can be expressed as follows:

$$R + [TPK] \rightarrow [TPK] \cdot R \tag{5}$$

$$[TPK] \cdot R + R \rightarrow [TPK] + R_2, \tag{6}$$

where *R* - active center (radical, atom) taking part in the chemical reaction;

R_2 - last product of the recombination reaction of radicals on the surface of a crystal of the salt-inhibitor;

[*TPK*] is a zone of the active part of the touched surface of a salt crystal.

Thus the process of the recombination of radicals at the time of inhibition represents the continuation if three molecular reactions that can be observed as a reaction consisting of two stages of biomolecular reactions. During the first stage a radical can make an intermediate product (5) with the salt-inhibitor. Then this radical reacts with one more radical on the surface of the salt crystal creating low-activity reaction products (6). So we can suppose that the chemical factor of salt activity – F is a function of speed of the reaction of radical recombination on the surface of salt inhibitor crystals:

$$F = \varphi(\omega), \tag{7}$$

where ω - surface recombination rate of the radicals on the salt-inhibitor crystal.

It is necessary for the radicals to interact with the hard salt part for the realization of the radical recombination on the crystal surface. According to (2) the quantity of interaction of radicals with the unit of the salt surface in a period of time dt is equal to:

$$dZ_R = (\frac{m}{2\pi kT})^{0,5} \cdot n \cdot u_p \cdot e^{-\frac{m \cdot u_p^2}{2kT}} \cdot du_p \cdot dt, \tag{8}$$

where Z_R - quantity of interaction of radicals with a unit of surface of a crystal in a period of time;

n - quantity of radicals taking part in the process;

m - mass of radical;

u_p - velocity of radical movement;

T - absolute temperature;

k - the Boltzmann constant.

The integration of the equation (8) using u_p from 0 to ∞ with ascription of impingement quantity to the unit of the time gives such an equation:

$$Z_R = (\frac{kT}{2\pi m})^{0,5} \cdot n.$$

According to [2] the average radical velocity depends on the temperature and can be defined as:

$$u_p = (\frac{8kT}{\pi m})^{0,5}.$$

So it is easy to take the quantity of interaction of radicals in a unit of the surface of a salt crystal for the period of time:

$$Z_R = \frac{u_p \cdot n}{\varphi}. \tag{9}$$

The probability of the recombination reaction – P depends on the quantity of impingements Z_R and on the orientation of the moving radicals in the zone of active section of the reaction on the surface of the salts crystal – σ_p. The quantity of such parts on the surface is equal to n_S. Its total square on the crystal surface is equal to

$n_S \cdot \sigma_p$. In this case the variety of the radicals interaction on the active part of the surface is equal to $P \cdot n_S \cdot \sigma_p$. Then the variety of the recombination reaction – W on the crystal surface of salt-inhibitor is equal to:

$$W = n_S \cdot \sigma_p \cdot p \exp[-\frac{E_a}{RT}], \tag{10}$$

where E_a - energy of activation of the recombination reaction;

R - the gas constant.

The velocity of the reaction on the surface of a crystal is equal to:

$$\omega = \frac{u_p \cdot n \cdot W}{4},$$

The velocity of the reaction for all surfaces of the salt parts – S that are situated in the volume of gas surrounding – V where the radicals are moving in the direction of these surfaces is equal to:

$$\omega = \frac{u_p \cdot n \cdot W}{4} \cdot \frac{S}{V}. \tag{11}$$

The active parts must be excluded from the zone of the reaction by their recombination on the surface of the salt-inhibitor for stopping of the chain reaction. The magnitude W, which maximally approaches unity, meets these conditions. In this case the velocity of the recombination reaction is of maximum importance on the surface of a salt crystal. The chemical factor of the activity of the salt-inhibitor is defined as follows:

$$F = \varphi(\omega) = n \cdot S \cdot const, \tag{12}$$

where $\frac{u_p \cdot W}{4V} = const$.

According to the advised scheme of the chemical recombination process it is necessary to take into account that the development of the transformation chain in the methane oxidation reaction takes place with the help of three types of active centers. These are radicals: hydrogen atoms – H and oxygen atoms – O, and hydroxyl radical – OH. As a result the chemical factor of the salt-inhibitor activity will depend on the prevailing type of radicals that takes part in the process of the development of ignition of the air-methane mixture. Therefore the equation (12) with *const* can be noted as:

$$F = n_i \cdot S, \tag{13}$$

where n_i is the prevailing quantity of one or another type of radicals taking part in the recombination process.

The question of the identification of the radical type at the time of the recombination is very important. The hydroxyl radicals and the hydrogen atoms have one valence-saturated connection, but atoms of oxygen have two valence-saturated connections. Thus it is necessary for the recombination of the corpuscular oxygen to use twice as many centers on the surface of crystals of the salt-inhibitor. Nowadays it is universally recognized that the best inhibitors of methane inflammation are halogenides of alkaline metals and the mechanism of their

interaction (particularly at the time of using safe explosives) turns into the breakage of the chains by the salt where the metal is responsible for the catalytic stopping action [3,4]. Thus we can estimate the meaning of n_i in the equation (13) at the time of the radical recombination by the salts that contain metal according to the next equation:

$$n_i = \frac{B_M \cdot N_a}{B_R}, \tag{14}$$

where B_M - metal valence;

N_a - quantity of metal atoms in salt;

B_R - quantity of valence-saturated connections of radical.

ANALYTICAL INVESTIGATIONS

The estimation of inhibition's activity of salt-inhibitors that are represented by halogenides of alkaline, land-alkaline and other metals under the condition that *S=const* in their salts is shown in the table 1.

Table 1 – Estimation of inhibition activity of salts

Salt Inhibitor air-methane mixture	Molecular weight	Quantity of metal atoms in a salt molecule, N_a	Metal valence, B_M	Radicals proportions			
				hydrogen ($\dot{H}$), hydroxyl ($\dot{O}H$)		elemental oxygen ($\dot{O}$)	
				F	$I \cdot 10^2$	F	$I \cdot 10^2$
LiF	25,94	1,0	1,0	1,0	3,855	0,5	1,927
LiCl	42,39	1,0	1,0	1,0	2,359	0,5	1,180
NaF	41,99	1,0	1,0	1,0	2,382	0,5	1,191
NaCl	58,44	1,0	1,0	1,0	1,711	0,5	0,8555
KCl	74,56	1,0	1,0	1,0	1,341	0,5	0,670
KF	58,1	1,0	1,0	1,0	1,721	0,5	0,860
CaF_2	78,0	1,0	2,0	2,0	2,564	1,0	1,282
$CaCl_2$	111,0	1,0	2,0	2,0	1,802	1,0	0,901
MgF_2	62,31	1,0	2,0	2,0	3,209	1,0	1,604
$MgCl_2$	95,22	1,0	2,0	2,0	2,10	1,0	1,05
AlF_3	83,98	1,0	3,0	3,0	3,5723	1,5	1,786
$AlCl_3$	133,34	1,0	3,0	3,0	2,2499	1,5	1,125
TiF_4	123,89	1,0	4,0	4,0	3,229	2,0	1,6145
$TiCl_4$	189,71	1,0	4,0	4,0	2,101	2,0	1,05

The inhibition activity of salt can be defined by the equation (2), taking into account the equations (13) and (14):

$$I = \frac{F \cdot S}{M_B} = \frac{B_M \cdot N_a}{B_R \cdot M_V} \cdot S. \tag{15}$$

The results of the calculation show that the inhibition activity of salts is in a good compliance with the results of the experimental works which are summarized in the report [5] being dedicated to this question. It is significant that the sodium chloride and the potassium chloride (the most widely used inhibitors in the modern permissible explosive mixtures) are not effective enough and are yielded to salts of lithium, magnesium, titanium, aluminum more than twice according to this index. It is significant that the inhibition activity of salts sharply goes down in case that the elemental oxygen is a prevailing active center in the zone of the reaction at the time of the chain branching reactions of the methane oxidation – poor air-methane mixtures or permissible explosives with a big positive oxygen balance. Many inhibitors remain ineffective under these conditions. Thus it was advised to use at least two-inhibitor combination in permissible explosives, where one inhibitor takes effect on the elemental hydrogen and hydroxyl and the other takes effect on the elemental oxygen. So it was determined that the recombination of the elemental oxygen went on effectively on the surface of crystals that were represented by oxalates and formats of the alkaline metals. The interaction of the elemental oxygen with the oxalates and formats of the alkaline metals went on in accordance with the scheme of the reaction:

$$Na_2C_2O_4 + \ddot{O} \rightarrow Na_2O + 2CO_2, \text{ and } NaCHO_2 + \ddot{O} \rightarrow NaOH + CO_2.$$

The sodium salts (oxide and hydroxide) being formed during the reaction are the effective inhibitors of the air-methane mixture.

CONCLUSIONS

As a result of the executed research it is necessary to note:

1. The recombination process of active centers on the salt-inhibitor crystal surface is considered in this work.

2. It was determined that each salt that is the inhibitor of the methane oxygen reaction is characterized by the chemical factor of activity.

3. The chemical factor of activity of salt- inhibitor has an elective character depending on the type of active centers that take part in the recombination process.

4. The inhibition activity of salts goes down appreciably if the active centers (elemental oxygen) take part in the recombination process.

5. It is advised to use the combined inhibitors consisting at least from a two-salt inhibitor as a new safety explosive mixture. One salt is intended for effective realization of the recombination of radicals of hydroxyl and elemental oxygen, and the other – for realization of the recombination of the elemental oxygen.

ZÁVĚR

K výsledku provedeného výzkumu je nutné poznamenat:

1. V této práci se posuzuje rekombinační proces aktivních center na povrchu krystalu soli inhibitoru.

2. Bylo zjištěno, že každá sůl, která je inhibitorem reakce metanu s kyslíkem, je charakterizována chemickým faktorem aktivity.

3. Chemický faktor aktivity soli jako inhibitoru má volitelný charakter v závislosti na typu aktivních center, které se účastní rekombinačního procesu.

4. Inhibiční aktivita solí se značně snižuje, pokud se rekombinačního procesu účastní aktivní centra (atomární kyslík).

5. Doporučuje se použít kombinované inhibitory, sestávající minimálně ze dvou solí, jako novou bezpečnou trhací směs. Jedna sůl je určena pro efektivní realizaci rekombinace radikálů hydroxylu a atomárního kyslíku a druhá pro realizaci rekombinace atomárního kyslíku.

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